

Thermodynamics of Conversion of Methane Clathrate Hydrate to Carbon Dioxide Hydrate Within Porous Media

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INTRODUCTION

Environmental concerns about rising concentrations of atmospheric carbon dioxide are stimulating R&D on a variety of carbon dioxide sequestration options. In energy-supply research, it has been estimated that natural gas hydrates in arctic and seafloor formations contain more energy than all other fossil fuel deposits (coal, oil, and natural gas) combined.¹ From data in the literature it is known that the conversion of bulk methane hydrate to bulk carbon dioxide hydrate is thermodynamically favored.¹ Thus, it has been proposed that the sequestration of CO₂ and the production of natural gas might be performed simultaneously by the injection of carbon dioxide into deposits of natural gas hydrates and the conversion of CH₄ hydrate to the hydrate of CO₂.^{2,3}

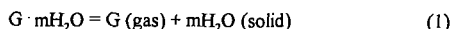
However, natural gas hydrates usually are found distributed within the pores of sediments,¹ and the thermodynamic parameters of methane hydrate are affected by the size of the pores in which the hydrates form.⁴⁻⁶ Recently we have measured the temperature-pressure equilibria and heats of formation of CO₂ hydrates in silica gel of various pore diameters. These measurements show how the temperature-pressure equilibrium of CO₂ hydrate depends on the pore size, and allow us to estimate the effect of pore size on the heat of dissociation of CO₂ hydrate. Bulk natural gas hydrates almost always occur in the "sII" crystal structure, because the presence of as little as one percent propane is sufficient to change the structure from the "sI" form of pure methane hydrate.¹ Measurements on the formation of hydrate(s) in pores by various multi-component natural gases have not yet been performed. Nevertheless, by comparing thermodynamic data for hydrates of CO₂ and CH₄ in porous media, we can explore whether calculations performed for the conversion of bulk natural gas hydrate to bulk carbon dioxide hydrate need to be corrected for pore-size effects.

EXPERIMENTAL METHOD

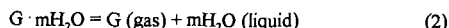
Carbon dioxide hydrate was synthesized within the pores of silica gel following the method described by Handa⁶ for hydrates of methane and propane. The silica gel was obtained from Aldrich; according to the vendor, the pore diameter of the Davisil™ material was 15.0 nm. Pore diameter and surface area also were determined by the BET method.⁷ The mesh size of the silica gel was 200-425, and the purity of the carbon dioxide (Matheson Coleman) was 99.99%. Sample temperatures were established by immersing the pressure cell in the fluid of a NesLab model RTE-140 chiller bath, which kept the temperature constant to within 0.05 K. Bath temperatures were read with a Hart Scientific model 1006 MicroTherm thermometer, traceable to NBS standards, with a sensitivity of 0.001 K. Pressures were measured by means of a calibrated Serta pressure transducer and readout with a sensitivity of 0.0068 MPa and an accuracy of 0.11% of full scale (20.40 MPa).

RESULTS

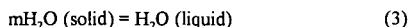
Figure 1 illustrates the equilibrium pressure vs. temperature curves for the hydrates of carbon dioxide (present work) and methane⁶ in 15 nm diameter pores. The carbon dioxide pressure-temperature data were converted to fugacities⁸ and plotted vs. 1000/T (Fig. 2). The carbon dioxide hydrate data in Figs. 1 and 2 are for two different equilibria:



and



where G is the "guest" molecule. Reactions (1) and (2) are in equilibrium at the (lowest) quadruple point. Linear regressions were performed to the data of Fig. 2 above and below the quadruple point, respectively. The regression equations were $\ln f = 17.671 - 4.7237/T$ ($R^2 = 0.9992$) and $\ln f = 18.184 - 4.8599/T$ ($R^2 = 0.9927$), respectively. The quadruple point (i.e., point of intersection of the two regressions) was $T_Q = 266.9$ K, $P_Q = 0.98$ MPa. As suggested by (1) and (2), the quadruple point determined by the equilibrium



is essentially independent of pressure over the change of quadruple point pressure induced either by pore effects or by changes of the "guest" component (CO_2 or CH_4). Hence, the quadruple point temperature is principally determined by the effect of pore size on the melting point. Using differential scanning calorimetry, Handa measured the melting point of ice in 15 nm diameter pores to be 267.5 K.⁹ Thus, the value for the quadruple point temperature found from the carbon dioxide hydrate data compares favorably with the expected value. From Handa's pressure-temperature data for methane hydrate we calculate $T_Q = 267.4$ K. The quadruple point temperature is $T_Q = 273.1$ K for bulk hydrates of CO_2 and CH_4 . Thus, the effect of pore size on the quadruple point temperature is simple: it is essentially the same for all guest-molecule compositions. For 15 nm diameter pores, the quadruple point temperature is lowered by 5.6 K.

Next, the enthalpies for equilibria (1) and (2) were estimated from the data plotted in Fig. 2, by means of the Clausius-Clapeyron equation. As listed in Table 1, these calculations yielded the values 35.59 kJ/mole for equilibrium (1) and, 39.10 kJ/mole for equilibrium (2) of CO_2 hydrate. Also listed in Table 1 are the enthalpies that we have calculated from Kamath's data for methane and carbon dioxide hydrates in sand packs¹⁰ and calorimetric data by Handa⁵ for methane hydrate in 15 nm silica gel. Additional data for CO_2 hydrates in porous media may be found in ref. 11.

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Table 1. Heats of Dissociation (kJ/mole) for Hydrates of Methane and Carbon Dioxide in Sand and in 15 nm Diameter Pores

Guest	Medium	Heat of Dissociation (kJ/mole)	
		reaction (1)	reaction (2)
CH_4	15 nm pores ^(a)	15.83	45.92
CH_4	sand ^(b)	15.22	68.84
CO_2	15 nm pores ^(c)	35.59	39.10
CO_2	sand ^(b)	25.43	82.43

^(a)Heat measured calorimetrically by Handa⁵

^(b)Heats calculated in the present work from the equilibrium pressure-temperature data of Kamath¹⁰

^(c)Heat obtained in the present work

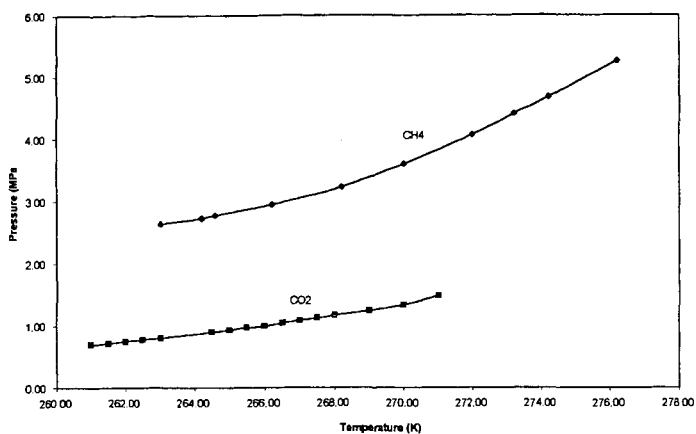


Figure 1. Equilibrium pressure-temperature for hydrates of CO₂ and CH₄ in 15 nm diameter pores of silica gel.

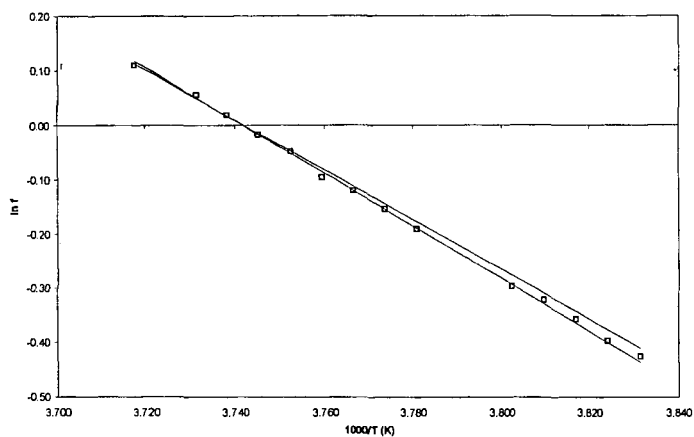


Figure 2. Logarithm of the fugacity, f , vs. inverse temperature, $1/T$, for CO₂ hydrate in 15 nm diameter pores of silica gel.